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Electrochemical Performance and Transport Properties of a Nafion Membrane in a Hydrogen-Bromine Cell Environment

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ELECTROCHEMICAL PERFORMANCE AND TRANSPORT PROPERTIES OF A NAFION

MEMBRANE IN A HYDROGEN-BROMINE CELL ENVIRONMENT

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SUMMARY

The overall energy conversion efficiency of a hydrogen-bromine energy storage system is highly dependent upon the characteristics and performance of the ion-exchange membrane utilized as a half-cell separator. This study has investigated the electrochemical performance and transport properties of a duPont Nafion membrane in an aqueous HBr-Br_2 environment. Membrane conductivity data are presented as a function of HBr concentration and temperature for the determination of ohmic voltage losses across the membrane in an operational cell. Diffusion-controlled bromine permeation rates and permeabilities are presented as functions of solution composition and temperature. Relationships between the degree of membrane hydration and the membrane transport characteristics are discussed. The solution chemistry of an operational hydrogen-bromine cell undergoing charge from 45 percent HBr to 5 percent HBr is discussed, and, based upon the experimentally observed bromine permeation behavior, predicted cell coulombic losses due to bromine diffusion through the membrane are presented as a function of the cell state-of-charge.

INTRODUCTION

The hydrogen-bromine fuel cell system has been a subject of considerable interest in recent years as a regenerative energy storage system and has been extensively investigated as an attractive technology for large-scale terrestrial energy storage (refs. 1 to 4). When coupled with a photovoltaic system to provide primary electrical power, the hydrogen-bromine system potentially is an attractive candidate for space power applications for which relatively high energy efficiencies are required.

One concept for an electrochemically regenerative hydrogen-bromine system employs a multicell configuration in which each electrochemical cell can be utilized for both charge and discharge operations. For each individual cell, a cation-exchange membrane is used to separate the negative half-cell, which contains a catalyzed hydrogen electrode and flow passages for gaseous hydrogen, from a positive bromine half-cell containing a porous carbon flow-by electrode and flowing aqueous hydrobromic acid (HBr) as an electrolyte.

In the charge mode, concentrated hydrobromic acid is electrolyzed. Bromine is formed at the positive electrode, and it remains solubilized in the aqueous electrolyte until it reaches its solubility limit. The solubilization of Br_2 is enhanced in bromide electrolytes by the formation of complex ions, and under usual cell operating conditions most of the Br_2 is present as the complex tribromide anion (Br_3^-), as expressed by the equilibrium (ref. 5)
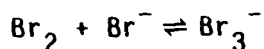
$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad\qquad K \simeq 16 \qquad\qquad (1)$$

where K is the equilibrium constant for the reaction. Thus, the reaction occurring at the positive electrode during charging can be represented by

$$3Br^-(aq) \rightarrow Br_3^-(aq) + 2e^- \tag{2}$$

Hydrated protons are transported across the membrane, and hydrogen gas is formed at the negative electrode according to the reaction

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \tag{3}$$

The hydrogen and bromine formed during the charge mode are stored external to the cell, and they are fed back to the cell during the discharge (fuel cell) mode to produce electrical energy. The overall cell reaction can be expressed stoichiometrically as

$$2H^+(aq) + 3Br^-(aq) \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} H_2(g) + Br_3^-(aq) \tag{4}$$
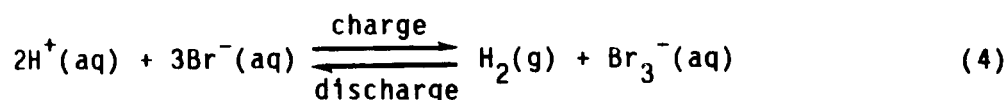
The attractiveness of the hydrogen-bromine system as a viable energy storage system is largely due to the thermodynamic reversibility of the hydrogen and bromine electrode reactions. The electrode reversibility results in a high electric-to-electric efficiency, as compared to projected efficiencies for other fuel cell systems (e.g., hydrogen-oxygen) (ref. 6).

Advances in membrane technology and the utilization of solid polymer electrolyte (SPE) fuel cell technology have resulted in the design of practical hydrogen-halogen cells which can operate at current densities in the range of 300 mA/cm^2 (ref. 7). Improved membrane electrochemical performance and stability, improved electrocatalysts, and the development of polymer-bonded electrodes have overcome mass transfer limitations which were inherent in the earlier low current devices (refs. 8 to 10).

Since the electrode kinetics of the hydrogen-bromine cell are fast, the voltage efficiency of the cell is determined by the ohmic resistance of the membrane, and coulombic losses can be attributed to the permeation of the Br_2-containing species[1] through the membrane. Both of these membrane performance factors are strongly related to the amounts of aqueous HBr and water which are absorbed by the membrane, and, hence, they will vary with changes in the bulk aqueous phase HBr concentration, as well as with changes in the cell temperature, during the charge and discharge cycles.

A schematic representation of the mass transport of the predominant species across the membrane during the discharge mode is shown in figure 1. Losses in current efficiency arise when Br_2 or Br_3^- react chemically with the hydrogen in the hydrogen electrode compartment, thus resulting in self-discharge. Hydrogen electrode poisoning by anion adsorption and degradation

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[1]In this paper, the expressions "Br_2-containing species" and "bromine" are used interchangeably to refer to molecular bromine, Br_2, and/or the anionic complex, Br_3^-.

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of the hydrogen electrode catalyst by reaction with Br_2 or Br_3^- also contribute to a deterioration in cell performance.

In order to achieve maximum efficiency and sustained performance over a long duration from an operational hydrogen-bromine fuel cell system, an ideal ion-exchange membrane would possess the following characteristics: (1) high chemical stability with respect to degradation by Br_2 in a highly acidic environment, (2) high proton conductivity, (3) low permeability to Br_2-containing species, and (4) a low permeation rate for bulk liquid or gas. Several studies have shown that a perfluorinated sulfonic acid membrane such as Nafion possesses the desired stability and adequate transport properties for utilization in hydrogen-halogen cells (ref. 2).

Nafion membranes, which are produced and marketed by the E.I. du Pont de Nemours and Company (Wilmington, DE), are chemically inert and are highly permeable to cations, while they effectively inhibit negative ion migration. The physicochemical properties, morphology, and transport properties of Nafion have been extensively investigated (refs. 11 to 14), and Nafion and similar perfluorinated ionomeric membranes are widely employed in a variety of electrolytic devices, including hydrogen-oxygen fuel cells and electrolyzers based on SPE technology (ref. 15). The results of several investigations of the transport properties of Nafion membranes with respect to their utilization in hydrogen-halogen cells (refs. 7 and 16) and in zinc-bromine cells (ref. 17) indicate that coulombic losses attributable to halogen diffusion should be low (<3 percent at 25 °C) in a practical halogen-based energy storage system.

The objective of the present study was to investigate the electrochemical performance and transport properties of a Nafion membrane in a chemical environment analogous to that encountered in a hydrogen-bromine fuel cell. Experimentally, measurements of the membrane resistivity and of the membrane permeation parameters and permeation fluxes for Br_2-containing species diffusing through the membrane were made in HBr media over the acid concentration range encountered in an operational cell. The effect of temperature on these performance parameters was also investigated. The data obtained from these measurements can be utilized for the determination of cell voltage and current efficiencies and are, thus, essential for an assessment of the viability of a hydrogen-bromine energy storage system for specific applications and for the optimization of cell components and system designs. The experimental measurements carried out are also applicable for the screening and characterization of alternative membrane candidates.

EXPERIMENTAL

Membranes

All measurements for this study were made on duPont Nafion-120 cation-exchange membranes. These unreinforced membranes have a thickness of ~0.025 cm in the dry state and an equivalent weight (EW) of 1200. The EW is defined by

$$IEC = 1000/EW \qquad (5)$$

where IEC is the ion-exchange capacity expressed in milliequivalents per gram of dry acid-form polymer.

All membrane samples were pretreated as follows in order to control the water content in the membrane and to insure reproducibility of the measurements. Samples were first fully converted to the acid form by equilibration with a dilute HBr solution containing a 30-fold milliequivalent excess, as based on the IEC, of hydrogen ions. Imbibed aqueous HBr was removed by repeated leaching in deionized water. The acid-form membranes were then boiled in water at 100 °C for 1 hr. As a result of this procedure, the membrane will absorb a specific amount of water while remaining immersed in water at room temperature, unless the effect is destroyed by drying at elevated temperatures (ref. 18). The amount of absorbed water will decrease upon exposure of the membrane to HBr solutions of increasing concentration.

Hydrated membrane thicknesses were measured at room temperature with a micrometer thickness gauge. Various degrees of hydration and swelling were achieved by equilibrating a membrane sample for several days with aqueous HBr electrolyte solutions which spanned the concentration range of interest.

Chemicals

All chemicals were of reagent grade and were used without further purification. Electrolyte solutions were prepared with deionized water. For the preparation of Br_2-free electrolyte solutions, care was taken to avoid air oxidation of the concentrated hydrobromic acid stock solutions which were employed by blanketing with nitrogen gas. The purity of the nitrogen gas employed for solution blanketing and sparging operations was higher than 99.9 percent.

Analytical Procedures

Volumetric analyses of Br_2-free and Br_2-containing HBr electrolyte solutions were routinely performed during this study. The concentrations of the equilibrated species present in a specific cell electrolyte being investigated were determined after withdrawal of a sample aliquot from the appropriate cell compartment at the appropriate time during the course of a measurement. The concentration of total bromine (molecular bromine, Br_2, plus the ionic complex, Br_3^-) was determined by iodometric titration with a standardized sodium thiosulfate solution. The total hydrogen ion concentration of the sample was then determined by titration against a standard base. The densities of some of the three-component solutions (Br_2-HBr-H_2O) were also measured for conversion to molal concentration units.

Laboratory Cell

All experimental measurements for the electrochemical performance evaluations and transport studies were conducted in a specially designed and fabricated two-compartment cell. The design criteria for the overall cell and experimental system included:

(1) The ability to perform both membrane conductivity and permeation measurements in the same cell configuration.

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(2) The ability to independently control and monitor the cell variables, such as temperature and electrolyte composition and concentration, in each half-cell.

(3) The ability to apply an external electric field across the membrane during the permeation measurements.

(4) The ability for dynamic electrolyte flow within each half-cell.

Due to the highly corrosive nature of the aqueous hydrobromic acid and bromine electrolyte, the laboratory cell was machined from Teflon TFE blocks, and all components in contact with the electrolyte were fabricated of either Teflon, glass, or noble metals. A schematic of the cell is shown in figure 2. Each half-cell, which is identified as cell A or cell B in figure 2, was fitted with a removable top plate, which contained Teflon PFA fittings for insertion of the various cell components. These components included a thermocouple well, a glass heating well containing a 100-W cartridge heater and silicone fluid as a heat transfer medium, a gas dispersion tube for solution sparging, an optional glass condenser, and working and auxiliary electrodes. Three of the electrodes were made of iridium wire and placed in separate compartments, connected to the rest of the cell by porous glass frits. Each half-cell also contained a Teflon stirring bar which was coupled magnetically to an external constant speed motor, a reference electrode well, and a 3-way Teflon stopcock selector valve for electrolyte sampling and flow control. The membrane, which had an exposed surface area of 5.07 cm^2, was sealed between each assembled half-cell using Armalon (Fairprene Industrial Products Co., Fairfield, CT) gaskets and a clamping arrangement. These inert gaskets were comprised of a Teflon fiber felt impregnated with Teflon TFE resin. A photograph of the assembled cell and its components is shown in figure 3.

The capability for external electrolyte storage and independent recirculation of electrolyte through each half-cell was also provided in the overall experimental system design. The desired electrolyte solutions for each half-cell were stored in separate glass reservoirs which were water-jacketed for maintaining desired temperatures. Solutions from the reservoirs were recirculated through the cell compartments by an all-Teflon pump (Fluorocarbon, Anaheim, CA) and valve system.

Conductivity Measurements

Membrane conductivity determinations in HBr solutions were made using the dc method of Lander and Weaver (ref. 19). Voltage drop measurements were made with a Keithley Model 616 digital electrometer in a fixed cell geometry using two saturated calomel electrodes with capillary probes in abuttal to the membrane and two auxiliary electrodes for passing a constant current. The total measured voltage drop between the probe tips of the reference electrodes, ΔE, can be expressed as

$$\Delta E = i_d[(RA)_M + (RA)_S] \tag{6}$$

where i_d is the current density (A/cm^2), and $(RA)_M$ and $(RA)_S$ are the areal resistances (Ω-cm^2) of the solution-equilibrated membrane and of

the thin layer of free electrolyte on both surfaces of the membrane, respectively. Values of $(RA)_S$ were experimentally determined in the same fixed cell geometry from "membrane-free" voltage drop measurements in aqueous HBr electrolytes at relevant concentrations and temperatures. The membrane resistivity, ρ_M, which is the inverse of the membrane conductivity, σ_M, was calculated from $(RA)_M$ by the expression

$$\rho_M = \frac{(RA)_M}{\ell}$$ (7)

where ℓ is the hydrated membrane thickness (cm), and ρ_M has the dimensions of Ω-cm.

Membrane resistivity measurements were made over a 1.0 to 7.5M HBr concentration range, and the temperature dependence of the conductivity was studied in the 20 to 60 °C range. The membrane, which had been pretreated as described previously, was equilibrated with the HBr solution for at least 24 hr prior to making a measurement. The membrane was then subjected to one heating cycle to 75 °C in the acidic electrolyte, prior to the measurements, in order to stabilize the membrane resistivity (ref. 20).

Permeation Measurements

The permeation of Br_2-containing species through the membrane was monitored by an electrochemical technique which was developed for the measurement of hydrogen permeation through metal membranes (ref. 21) and subsequently employed by Nanis and Wolf (ref. 22) to study ion permeation through battery separator material. This technique has also been used by investigators to measure the permeation of hydrogen and halogens (ref. 7) and oxygen (ref. 23) through Nafion. A schematic of the experimental cell arrangement is shown in figure 4. After bromine was introduced into the left-hand compartment, the permeation rate of the Br_2-containing diffusant (Br_2 and/or Br_3^-) was monitored by quantitatively reducing the halogen electrochemically as it came through the membrane. A 52-mesh platinum screen in abuttal to the membrane served as the working cathode for the halogen reduction; the counterelectrode, also on the diffusant-receiving side of the membrane, was isolated from the bulk electrolyte by a porous glass frit in order to inhibit the mass transport of its oxidation products towards the working electrode. The potential of the platinum screen cathode was maintained at 0.15V positive to the saturated calomel reference electrode (SCE) with a Princeton Applied Research Model 173 potentiostat. A polarization curve verified that the cathode potential was well within the diffusion-limiting current region for the relevant diffusant concentrations.

Well-defined initial and boundary conditions in the membrane were maintained by the sequence of operations used in carrying out the permeation measurements. Bulk electrolyte at the desired HBr concentration was added to both cell compartments, and equilibrium was established with the membrane prior to the permeation measurements. The electrolyte was then sparged with nitrogen gas, which was prehumidified to the same water activity as that of the aqueous electrolyte, in order to remove traces of dissolved oxygen. The potentiostat was turned on, and the stable residual current was monitored on an X-Y recorder (Esterline Angus Model XY 530) equipped with a time base. The electrolyte in the diffusant-containing cell compartment was drained, mixed with a Br_2-HBr

stock solution at the same HBr concentration as the bulk electrolyte, and quickly introduced back into the same compartment. Following an initial breakthrough period, a permeation current transient, which reflected the buildup of the concentration gradient within the membrane, was recorded. Thereafter, the permeation current reached a constant value, indicating a steady-state concentration profile within the membrane and a constant flux throughout.

After the achievement of steady-state permeation, an aliquot of electrolyte was removed from each cell compartment for analysis. Successive transients could then be recorded for increasing total bromine concentration, which was effected by the rapid addition of an aliquot of the Br_2-HBr stock solution to the diffusant-containing cell compartment. Measurements of steady-state permeation fluxes at various temperatures were carried out using internal cell compartment heaters for temperature control to within ±1 °C during a run.

RESULTS AND DISCUSSION

Cell Solution Chemistry

For a hydrogen-bromine cell with an aqueous Br_2-HBr solution in the bromine electrode compartment, the membrane conductivity and permeation behavior are both strongly dependent at any point in time upon the bulk solution concentration and composition. Changes in the external HBr concentration result in changes in the amount of aqueous HBr absorbed by the membrane and in the degree of membrane hydration, and these changes have a pronounced effect upon the membrane conductivity, diffusivity, and diffusant permeation rates. For a given degree of membrane hydration, the permeation flux for bromine through the membrane is also dependent upon the concentration of bromine in the external solution. As the concentration of external HBr in equilibrium with a Nafion membrane increases, the amount of solution absorbed by the membrane decreases and the HBr concentration inside the membrane increases (ref. 2).

The operation of a hydrogen-bromine system is a nonsteady-state process, and the bulk solution concentration and composition continuously changes with time, as shown by the overall cell reaction (eq. (4)). During the charge cycle, the external HBr concentration will decrease as bromine is formed by electrolysis. Accordingly, both the amount of HBr solution absorbed by the membrane and the degree of membrane hydration will increase with time during charge.

Figure 5 shows the change in the molar concentration of HBr and of bromine in the bulk aqueous phase as a function of the cell state-of-charge (SOC) for the room temperature operation of a cell which is initially started with 45 percent HBr and then charged to 5 percent HBr. In this figure, c_B represents the total aqueous-phase bromine concentration based on the cell reaction stoichiometry and is irrespective of its actual chemical state. At ~86 percent state-of-charge, the solubility limit for bromine in this system is reached, and a second liquid phase consisting of elemental bromine is formed. This point of bromine phase separation and the aqueous-phase concentrations at states-of-charge greater than this point were calculated from available solution density data (ref. 24) and solubility data (ref. 25) for the HBr-Br_2-H_2O system. The solution density and the total number of milliequivalents of Br per gram of H_2O remain constant in the aqueous phase at states-of-charge below the bromine saturation limit.

The actual chemical state of the bromine in the bulk aqueous phase is governed by the equilibrium reaction expressed by equation (1). As bromine is formed in the concentrated HBr solution during the charge cycle, the Br_2 complexes with Br^- to form Br_3^-, which, as indicated by the magnitude of the equilibrium constant for the reaction, is the predominant Br_2-containing species in the bulk aqueous phase after equilibration.

The equilibrium concentrations of Br^-, Br_3^-, and Br_2 in the bulk aqueous phase were calculated over the charge cycle which is represented by the pre-equilibrium concentrations shown in figure 5. The three equilibrium concentrations are plotted in figure 6, and they were determined by simultaneously solving the following three equations:

$$K = \frac{[Br_3^-]}{[Br_2][Br^-]} \tag{8}$$

$$c_H = [Br^-] + [Br_3^-] \tag{9}$$

and

$$c_B = [Br_2] + [Br_3^-] \tag{10}$$

where the brackets denote equilibrium concentrations. Equation (9) represents the requirement for electroneutrality after equilibrium, and c_H is equal to the molar concentration of H^+ prior to equilibrium. In equation (10), the concentration of total Br_2-containing species after equilibrium, c_B, is equal to the total aqueous-phase Br_2 concentration prior to equilibrium. The concentration of free Br_2 in the aqueous phase attains values below 0.1 mol/liter for H^+ concentrations larger than 3.5M and exhibits a maximum at the bromine solubility limit. The $[Br_3^-]/[Br_2]$ ratio in the aqueous phase is greater than 100 at low states-of-charge and progressively decreases during the charge cycle. By the time the H^+ concentration falls to ~2M (i.e., ~84 percent SOC), this ratio has decreased by almost two orders of magnitude.

Membrane Conductivity

The results of the conductivity measurements on a Nafion-120 membrane in Br_2-free HBr at 25 and 50 °C are presented in figure 7 as the membrane specific resistance (or areal resistance) versus HBr concentration over the range indicated by figure 5. Presented in this form, the ohmic voltage loss across the membrane in an operational cell can be determined by simply multiplying the specific resistance, which is defined as the resistance for a 1 cm^2 area and a given thickness, by the cell current density. The point shown on the plot for the membrane specific resistance in pure H_2O at 25 °C was calculated by using equation (7) with the experimentally-measured hydrated membrane thickness and the literature value for the intrinsic conductivity of Nafion in pure water (ref. 26). The intrinsic conductivity of the membrane originates from the strong acidity of the fixed sulfonic acid groups.

The membrane exhibited a maximum conductivity of 0.073 $\Omega^{-1}cm^{-1}$ at 25 °C in ~3M HBr. This value is in excellent agreement with a semiempirically-calculated

literature value (ref. 2) of 0.077 $\Omega^{-1}cm^{-1}$ at a HBr concentration of 3M, which was also reported to be the point of maximum conductivity. The maximum in the conductivity is probably attributable to the trade-off between the low hydrogen ion concentration existing inside the membrane at low external HBr concentrations and the decreasing membrane water content at higher external HBr concentrations (ref. 7). As the membrane dehydrates, there is a decrease in the volume fraction of the membrane that supports ionic mobility.

The temperature dependence of the membrane conductivity is illustrated by the Arrhenius plots shown in figure 8 for the three experiments performed at HBr concentrations greater than 3M, which is the HBr concentration corresponding to the observed conductivity maximum. Since the degree of membrane hydration for each HBr concentration remained constant over the temperature range investigated as a result of the thermal pretreatment employed, the increase in conductivity on heating reflects an increase in ionic mobility within the absorbed aqueous phase. Activation energies for proton transport in the Nafion-120, which were calculated from the Arrhenius plots, are given in table I along with membrane conductivities for the various HBr concentrations examined.

The fast proton conduction in perfluorosulfonic acid membranes can be attributed to the strong hydrophilicity and acidic character of the fixed sulfonate (SO_3^-) groups and to the nature of the absorbed water, which is not as strongly hydrogen bonded in Nafion as it is in aqueous solutions (ref. 26). The observed low activation energies for proton transport, which are similar in magnitude to the energy for hydrogen bonding, are indicative of relatively weak interactions between the protons and the fixed ions as a result of the strong hydration of the sulfonate groups.

Analogous to results obtained for Nafion-120 in HCl media (ref. 7), an increase in the activation energy would be expected at high HBr concentrations, thus reflecting increased coulombic interaction between the ions as the membrane dehydrates. Calculations based on electrolyte uptake data (ref. 2) and consistent with the accepted ion-cluster morphology model for Nafion show that the number of H_2O molecules per SO_3^- group decreases from approximately 13.5 to 9 as the external HBr concentration increases from 3.9 to 7.3M. As shown in table I, only a slight increase in the activation energy was observed between these two HBr concentration values.

Bromine Diffusivity

The bromine permeation transients, which were observed as reduction currents by the experimental electropermeation method described previously, reflected diffusion through the membrane under a known set of initial and boundary conditions. These conditions in which the bromine concentrations (c) at the input (x = 0) and exit side (x = ℓ) of the membrane are known at various times (t) are:

$$c = c_0; \quad x = 0; \quad t \geq 0 \tag{11}$$

$$c = 0; \quad x = ℓ; \quad t \geq 0 \tag{12}$$

$$c = 0; \quad 0 < x < ℓ; \quad t < 0 \tag{13}$$

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Experimentally, the initial condition (eq. (13)) was verified by the presence of only a small residual steady-state background current prior to introduction of the bromine diffusant. During the transient, the bulk bromine concentration in the diffusant-containing cell compartment was kept constant, and a constant bromine concentration just inside the surface of the membrane at the input side (c_0) was assumed, thus satisfying equation (11). Equation (12) was fulfilled because the bromine was quantitatively reduced upon arriving at the monitoring electrode in abuttal to the exit side. This was verified by a steady-state plateau of the reduction current at the applied cathodic potential.

The overall diffusion process may be represented by Fick's second law:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{14}$$

where D is the diffusion coefficient, or diffusivity, within the membrane. The permeation flux (J) of bromine through the membrane is described by Fick's first law:

$$J = -D \frac{\partial c}{\partial x} \tag{15}$$

Using the boundary conditions stated above, Fick's second law equation can be solved with the aid of Laplace transforms, for example (ref. 20). The first-term approximation of the solution yields the following relationship for the ratio of J_t, which is the time-dependent permeation flux at $x = \ell$ and time t, to J_∞, which is the steady-state permeation flux at $t = \infty$:

$$\frac{J_t}{J_\infty} = \frac{2}{(\pi\tau)^{1/2}} \exp\left(-\frac{1}{4\tau}\right) \tag{16}$$

where $\tau = Dt/\ell^2$ is a dimensionless time parameter. This first-term approximation is valid up to $J_t = 0.965 \, J_\infty$. The theoretical curve of (J_t/J_∞) as a function of τ is shown as the solid line in figure 9.

In the steady-state condition a linear concentration gradient through the membrane is assumed and

$$J_\infty = \frac{D c_0}{\ell} \tag{17}$$

where J_∞ has the dimensions of moles-cm^{-2}-sec^{-1}. The steady-state flux can alternatively be expressed in terms of the steady-state current density, i_∞ (A/cm^2):

$$i_\infty = \frac{nFD c_0}{\ell} \tag{18}$$

where n is the number of electrons involved in the reduction reaction at the monitoring electrode, F is the Faraday constant, and D and c_0 are expressed as cm^2/sec and moles/cm^3, respectively. Equation (18) shows that the experimentally observed steady-state permeation current is expected to

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be proportional to the bromine concentration in the diffusant-containing cell compartment.

By fitting a normalized experimental curve of i_t/i_∞ (= J_t/J_∞) against time (t) with the theoretical permeation transient of figure 9, the "apparent"[2] bromine diffusivity in the membrane can be computed if the experimental results fit closely with the theoretical curve, thus indicating that the diffusional behavior of the system agrees with the postulated model. As an example, one set of experimental results obtained for the transient permeation behavior of bromine through a Nafion-120 membrane is plotted as the broken curve in figure 9. From equation (16), a value of J_t/J_∞ = 0.5 corresponds to τ = 0.138, and the value of D can be calculated from the definition of τ expressed as

$$D = 0.138 \frac{\ell^2}{t_{1/2}} \tag{19}$$

where $t_{1/2}$ is the half-rise time at which i_t/i_∞ = 0.5 on the experimentally obtained plot of (i_t/i_∞) versus t. Since the steady-state permeation flux can be measured directly, the value of c_0 can be calculated from equation (17) using the D value obtained from the transient analysis.

The experimental diffusivities for bromine in the specific Nafion-120 membrane sample under investigation are shown in figure 10 as a function of external HBr concentration. The expected decrease in bromine diffusivity with increasing HBr concentration was observed at HBr concentrations greater than ~3M; however, anomalously low values were observed at lower HBr concentrations. At the present time, no substantiated explanation can be given for the anomalous results. It is uncertain as to whether or not the observed decrease in the diffusivity as the HBr concentration decreased below ~3M was real for the particular membrane sample being investigated and its "pretreatment" history (e.g., the actual degree of membrane hydration), or whether the experimental conditions had an effect on the current transient response during the dilute HBr evaluations.

The calculated concentration of total bromine dissolved just inside the surface of the membrane at the input side, c_0, was significantly lower than the concentration of total Br_2-containing species in the bulk solution, c_B. Figure 11 shows the relationship of c_0 to c_B for bromine in 5.35M HBr at 25 °C. The difference between c_0 and c_B has been shown to be related to the formation of the complex Br_2-containing anions in bromide solutions (ref. 7).

Since the $Br_2/Br^-/Br_3^-$ equilibrium expressed by equation (1) is unknown within the membrane, it is impossible to differentiate between Br_2 and Br_3^- as

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[2]The computed value of the diffusivity is an "apparent" value in the sense that the mathematical formalism based on Fick's second law is not adequate to account for any dependence of D on the diffusant concentration (ref. 27). In the experimental investigation presented in this paper, the bromine diffusivity is assumed to be independent of the bromine concentration.

the actual diffusing species. However, it has been suggested (ref. 28) that Br_2, which is dissolved within the membrane, is more likely to be the species actually diffusing through the membrane structure. This suggestion is based upon considerations of the internal equilibrium: the relatively low Br^- concentration existing within an anionic membrane would cause the equilibrium between the bromine species to be strongly in favor of dissolved elemental Br_2.

Bromine Permeability

A practical and realistic way of expressing the overall degree of permeation through a membrane is by defining the permeability, Q, which is a phenomenological parameter related to the permeation flux by the experimentally measurable external concentration of the permeating species, c_B:

$$J_\infty = \frac{Qc_B}{\ell} \tag{20}$$

For the case in which the actual permeation mechanism is diffusion, equation (17) can be combined with equation (20) to show that the permeability depends upon the solubility as well as upon the diffusivity:

$$Q = D\frac{c_0}{c_B} \tag{21}$$

where the ratio c_0/c_B represents a distribution or partition coefficient of the diffusant between the membrane and the external bulk solution phases.

As the actual coulombic losses in an operational cell are determined by the product of the diffusivity or the permeability and the appropriate concentration term, a permeation factor, P, can be defined as

$$P = J_\infty\ell = Dc_0 = Qc_B \tag{22}$$

According to equation (22), if the HBr concentration is kept constant, a linear relationship would be expected between P and the concentration of total bromine in the external solution. This analysis assumes that the observed permeation behavior is governed by the aforementioned internal membrane equilibrium and is independent of the actual Br_2-containing species which exist in the bulk aqueous phase. Figure 12 is a plot of the experimentally observed bromine permeation factor at 25 °C as a function of the external total bromine concentration for various aqueous HBr concentrations. The permeation fluxes reflected by P are diffusional fluxes of Br_2 and Br_3^- only; the test cell configuration assured that no Br_2-containing species were transported through the membrane by electromigration.

The observed linearity shown in figure 12 between the permeation factor and the external total bromine concentration supports the assumption that the observed permeation behavior is irrespective of the actual Br_2-containing species present in the bulk aqueous solution phase over the bromine concentration range examined. Thus, the aforementioned coulombic losses and detrimental effects in an operational cell, which are attributable to membrane permeation by either Br_2 or Br_3^-, can be phenomenologically related to the measurable total bromine concentration, c_B. Experimentally, no linear dependence between

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P and the equilibrium concentration of Br_2 in the aqueous phase was observed as c_B was varied while the HBr concentration was held constant.

The slopes of the experimental plots shown in figure 12 yield the bromine permeabilities according to equation (22), and the linear relationship between permeability and external HBr concentration is shown in figure 13. The decrease in bromine permeability with increasing HBr concentration is primarily related to the permeation-inhibiting effects associated with membrane dehydration. As dehydration occurs, internal reorganizations of the ion-cluster morphology of Nafion occur, which result in narrower channels for diffusion. Also, the electrostatic potential energy barrier to anion migration increases as the membrane fixed charge density increases. The increase in the internal HBr concentration with increasing external solution concentration results in more pronounced ion association and increased viscosity of the imbibed solution, which would also contribute to lower bromine permeabilities (ref. 28).

As the permeation factor, P, is by definition the product of two temperature-dependent terms, D and c_0, the effect of temperature on the permeation flux can be described by the following Arrhenius-type relationship:

$$P = P_0 \exp\left(-\frac{E_p}{RT}\right) \tag{23}$$

where E_p is an apparent activation energy for permeation, R = 1.987 cal-mol^{-1}deg^{-1}, and T is the absolute temperature. In this equation, the energy parameter E_p is actually equal to the sum of the apparent activation energy for diffusion, E_D, and an energy parameter, E_S, which is related to the apparent heat of solution for bromine dissolution in the membrane phase.

The temperature dependence of the permeation factor, or of the bromine permeation flux through the Nafion membrane, is illustrated by the Arrhenius plot shown in figure 14 for a value of c_B = 0.23M in 5.22M HBr. The increase in bromine permeation with temperature is primarily associated with an increase in the diffusant mobility at elevated temperatures. Experimental values of E_p, calculated from Arrhenius plots, are given in table II along with the permeation parameters for various HBr concentrations.

The similar magnitudes of the observed values of E_p over the 2 to 7.5M HBr concentration range are probably attributable to opposing effects of HBr concentration on the parameters E_D and E_S. As the HBr concentration increases and the membrane becomes dehydrated, the bromine diffusivity decreases, and, thus, an increasing value of the energy barrier for diffusion, E_D, would be expected. However, as the solubility of bromine is higher in more concentrated HBr solutions, a decreasing value of E_S (i.e., an increasing value of c_0 for a constant concentration of total bromine in the external solution) would be expected as the HBr concentration increases.

Cell Coulombic Losses

Based upon an analysis of the experimentally observed membrane permeation behavior of bromine in an aqueous HBr environment, coulombic losses attributed to the diffusional migration of Br_2-containing species through a Nafion-120 membrane have been calculated for the operation of the hydrogen-bromine cell

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represented by figure 5. Bromine permeation fluxes were extrapolated to correspond to the actual concentrations of total bromine existing in the cell at various states-of-charge, and the effects of temperature on the resultant fluxes were evaluated. In figure 15, the bromine permeation currents through a Nafion-120 membrane are plotted as a function of the cell state-of-charge for both 25 and 50 °C operation of a cell being charged from 45 to 5 percent HBr.

As shown in figure 15, the bromine permeation current density and, thus, the cell coulombic losses reach a maximum value at the solubility limit for bromine in this system. At states-of-charge above the bromine solubility limit, the bromine permeability, Q, is assumed to continue to increase, however, the permeation flux decreases as a result of the rapid decrease in the aqueous phase concentration of total bromine, c_B. At low states-of-charge where the concentration of Br_2 in the aqueous phase is negligible, the cell coulombic losses are almost exclusively attributable to membrane permeation by Br_3^- from the bulk solution phase. The cell current efficiency is enhanced at the lower states-of-charge as a result of the electrostatic rejection of the Br_3^- species by the negatively charged polymeric membrane.

SUMMARY OF RESULTS

An integral part of an assessment of the viability of a hydrogen-bromine energy storage system for space power applications is the determination of the overall efficiency of the system, as well as a characterization of the system components with respect to stability and performance. With these objectives in mind, the electrochemical performance and transport properties of a Nafion-120 membrane have been investigated in a chemical environment analogous to that encountered in a hydrogen-bromine fuel cell. Membrane conductivities have been determined as a function of HBr concentration and temperature, and data have been presented for the determination of the ohmic voltage losses across the membrane in an operational cell.

Membrane permeation parameters and permeation fluxes for Br_2-containing species diffusing through the Nafion-120 membrane were determined in HBr media over a 1 to 8M acid concentration range, which would be encountered in a H_2-Br_2 cell, and as a function of temperature. The transport properties were found to be strongly dependent upon the degree of membrane hydration. The experimental electropermeation method employed for these studies can be utilized for the screening of membrane candidates in order to assess coulombic efficiencies, as well as for in-depth membrane characterizations.

The cell solution chemistry was discussed for the operation of a hydrogen-bromine cell which is initially started with 45 percent HBr and then charged to 5 percent HBr. The experimentally observed bromine permeation behavior was used to predict actual cell coulombic losses, which are attributable to bromine diffusion through the membrane, as a function of the state-of-charge for this hypothetical cell.

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TABLE I. - NAFION-120 MEMBRANE CONDUCTIVITIES AND ACTIVATION ENERGY FOR PROTON CONDUCTION IN BROMINE-FREE HBr ELECTROLYTE SOLUTIONS

HBr concentration		Hydrated membrane thickness, cm	Membrane conductivity, σ_M, Ω^{-1}-cm^{-1}		Activation energy for conduction,[a] kcal/mol
mol/liter	wt %		25 °C	50 °C	
1.34	10.2	2.89×10^{-2}	0.066	0.100	3.20
2.07	15.1	2.88×10^{-2}	.064	.103	3.49
3.88	26.0	2.84×10^{-2}	.070	.095	2.32
5.15	32.5	2.81×10^{-2}	.052	.070	2.20
7.32	42.2	2.76×10^{-2}	.026	.038	2.88

[a]Calculated from Arrhenius plots.

TABLE II. - EXPERIMENTAL BROMINE DIFFUSIVITIES AND PERMEABILITIES IN A NAFION-120 MEMBRANE AT 25 °C AND ACTIVATION ENERGY FOR PERMEATION FOR VARIOUS HBr CONCENTRATIONS

HBr concentration, mol/liter	Cell SOC,[a] %	Bromine diffusivity, D, cm^2/sec	Bromine permeability, Q, cm^2/sec	E_p,[b] kcal/mol
1.33	95.2	5.36×10^{-7}	---------	7.36
2.08	83.3	6.07×10^{-7}	1.45×10^{-7}	5.91
3.65	61.6	6.96×10^{-7}	1.22×10^{-7}	6.28
5.23	39.5	$^c5.68 \times 10^{-7}$	9.50×10^{-8}	6.21
7.40	8.9	3.97×10^{-7}	5.91×10^{-8}	5.70

[a]Corresponding state-of-charge of a H_2-Br_2 cell being charged from 45 to 5 percent HBr.
[b]Apparent activation energy for bromine permeation.
[c]Experimental diffusivity value for 5.20M HBr.
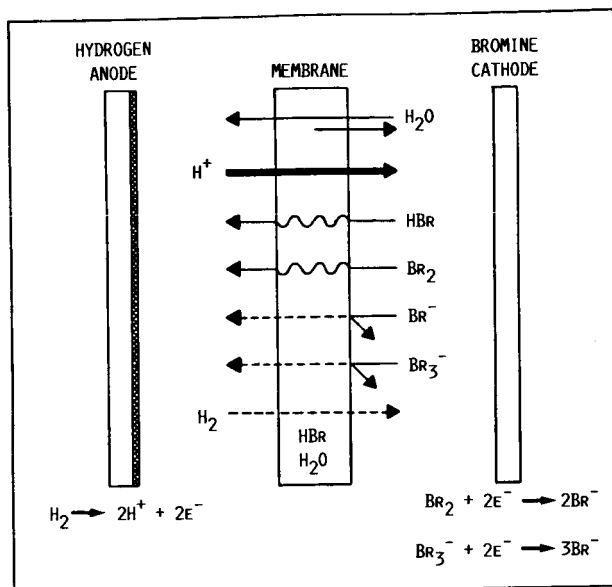
FIGURE 1. - MASS TRANSFER THROUGH A MEMBRANE DURING THE
DISCHARGE MODE OF OPERATION OF A HYDROGEN-BROMINE
CELL.
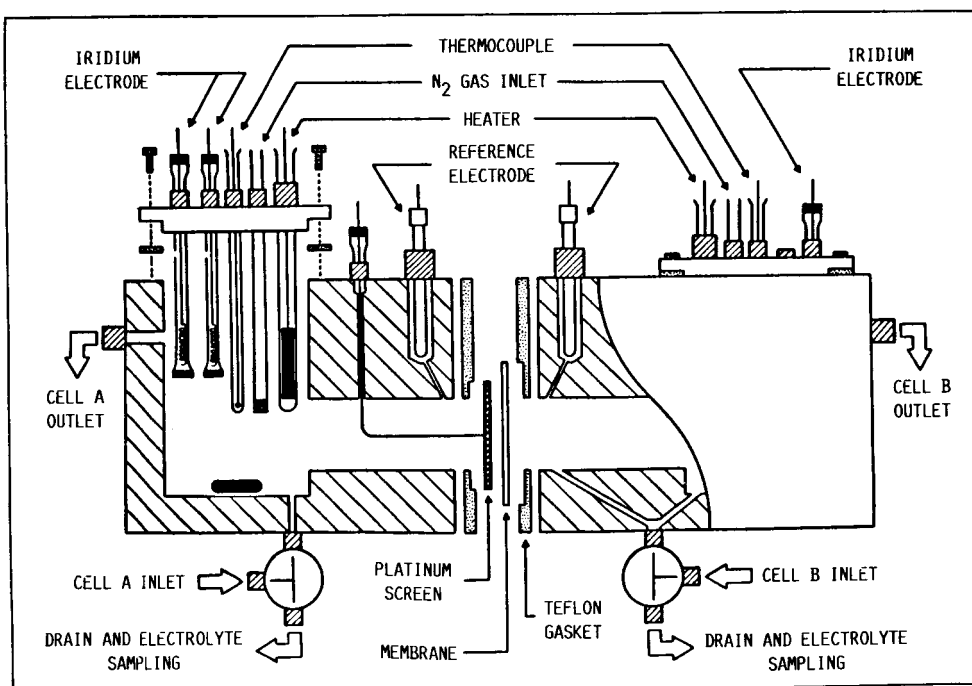
FIGURE 2. - DIAGRAM OF LABORATORY CELL FOR THE EVALUATION OF MEMBRANE TRANSPORT PROPERTIES AND
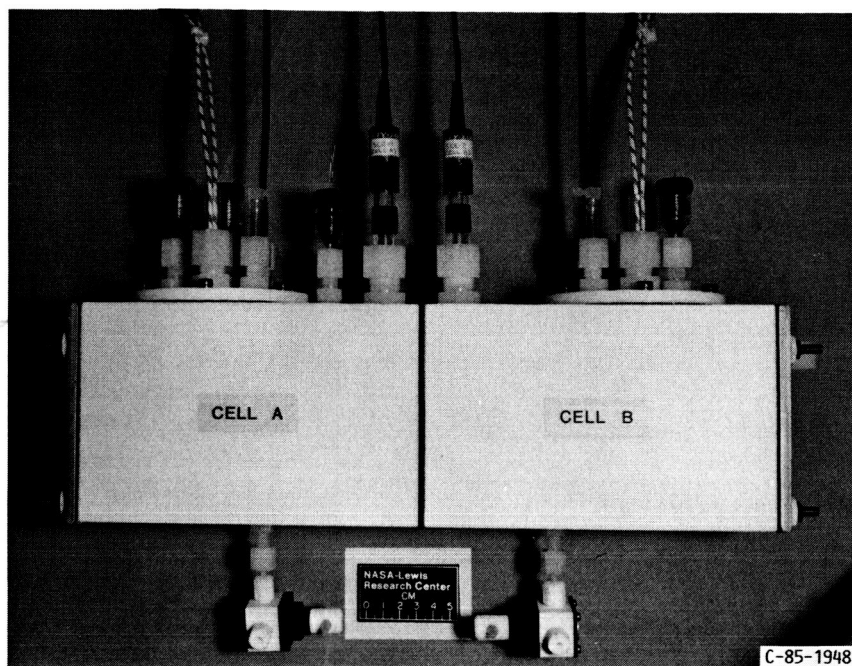ELECTROCHEMICAL PERFORMANCE.
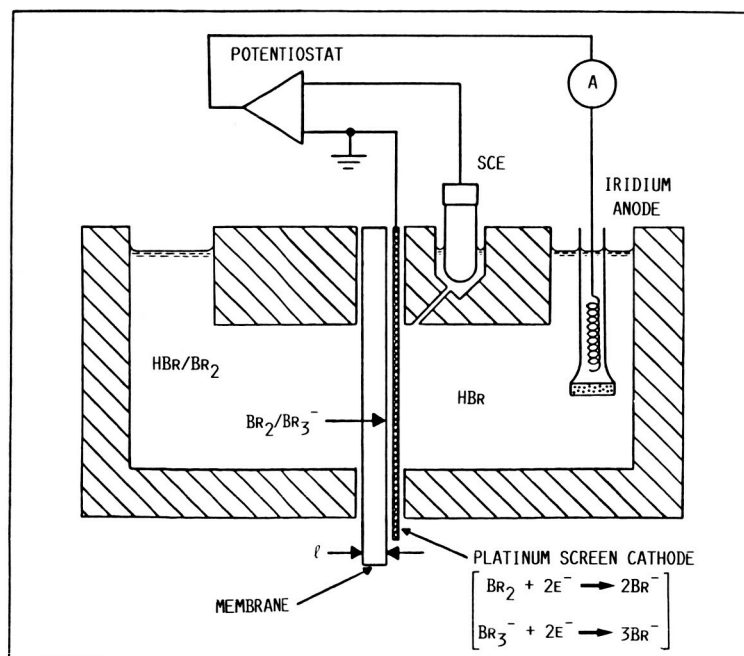
FIGURE 3. - ASSEMBLED MEMBRANE EVALUATION CELL.

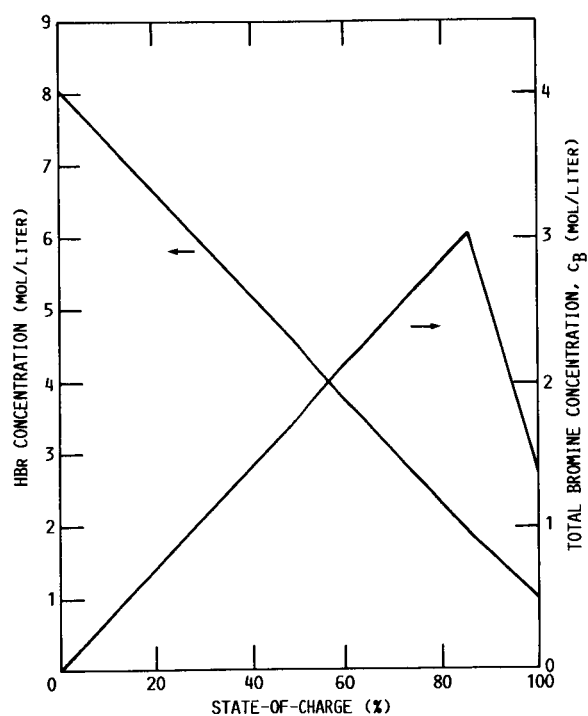FIGURE 4. - CELL ARRANGEMENT FOR BROMINE PERMEATION MEASUREMENTS.

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FIGURE 5. - CHANGES IN HBr AND TOTAL BROMINE CON-
CENTRATIONS IN THE BULK AQUEOUS PHASE DURING
THE CHARGE CYCLE OF A H_2-Br_2 CELL BEING CHARGED
FROM 45% HBr TO 5% HBr.
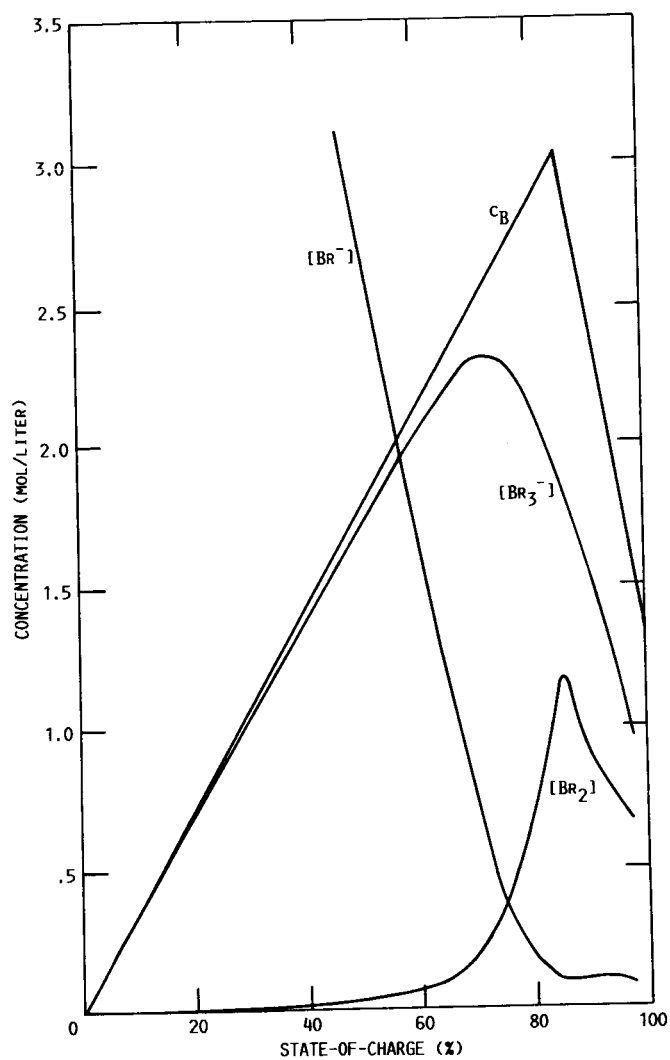
FIGURE 6. - CALCULATED EQUILIBRIUM CONCENTRATIONS OF Br^-,
Br_3^-, AND Br_2 IN THE BULK AQUEOUS PHASE AS A FUNCTION OF
STATE-OF-CHARGE OF A H_2-Br_2 CELL WITH TOTAL BROMINE CON-
CENTRATION c_B.

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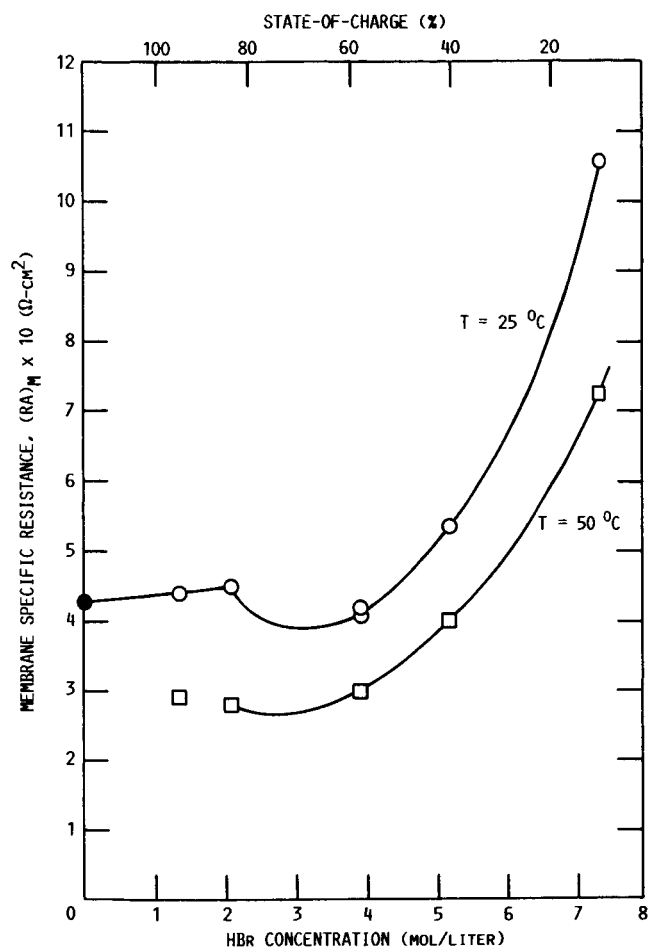
FIGURE 7. - SPECIFIC RESISTANCE OF NAFION-120 AS A FUNCTION OF HBr CONCENTRATION AND TEMPERATURE. (●) H_2O, FROM REF. 26.
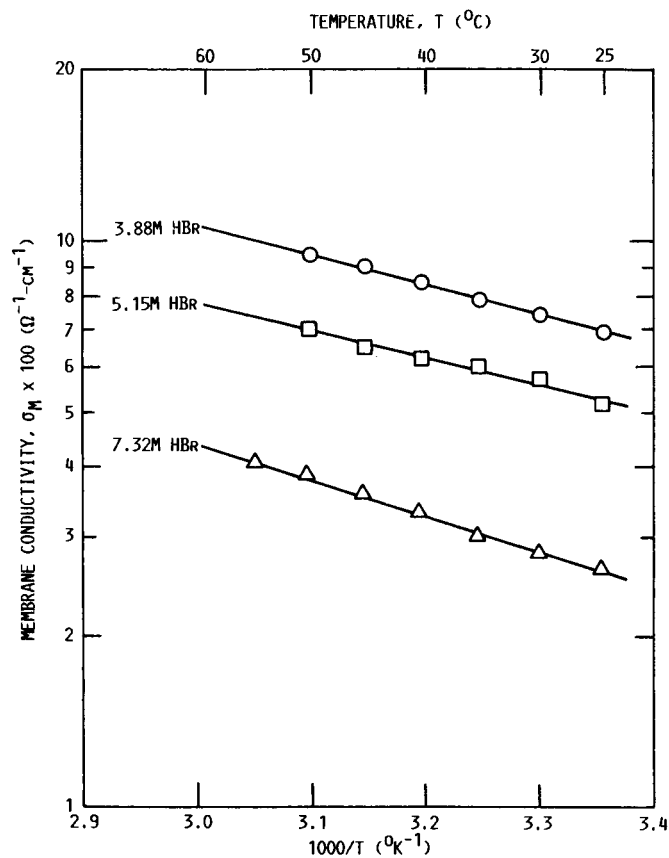
FIGURE 8. - ARRHENIUS PLOTS FOR NAFION-120 MEMBRANE CONDUCTIVITIES FOR VARIOUS AQUEOUS HBr CONCENTRATIONS.

TIME, t (SEC)
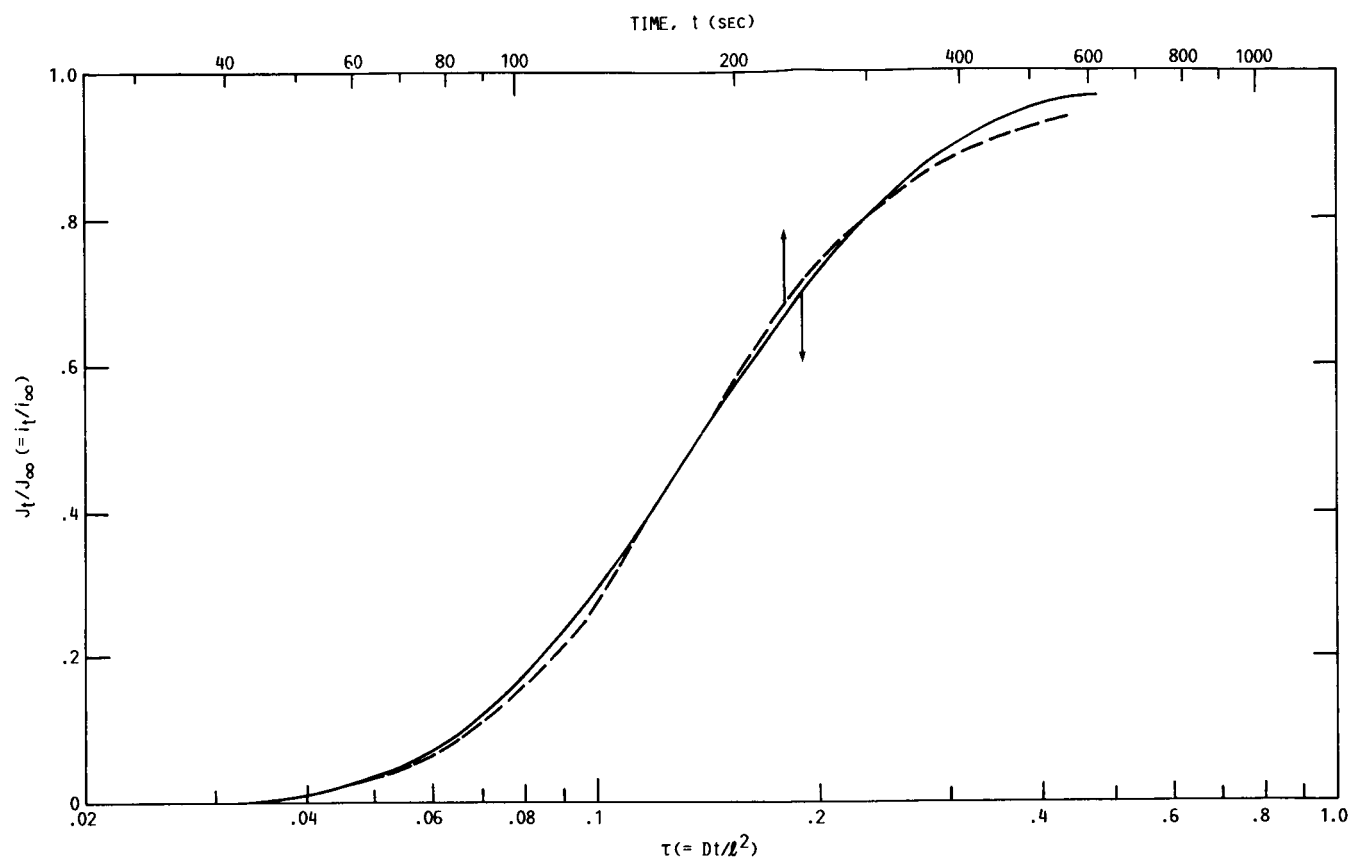
FIGURE 9. - BROMINE PERMEATION TRANSIENTS. SOLID LINE: THEORETICAL CURVE FROM EQ. (16). BROKEN LINE: EXPERIMENTAL RESULTS FOR PERMEATION THROUGH NAFION-120 AT 24 ^{O}C IN 3.62M HBr/0.26M BR$_2$.
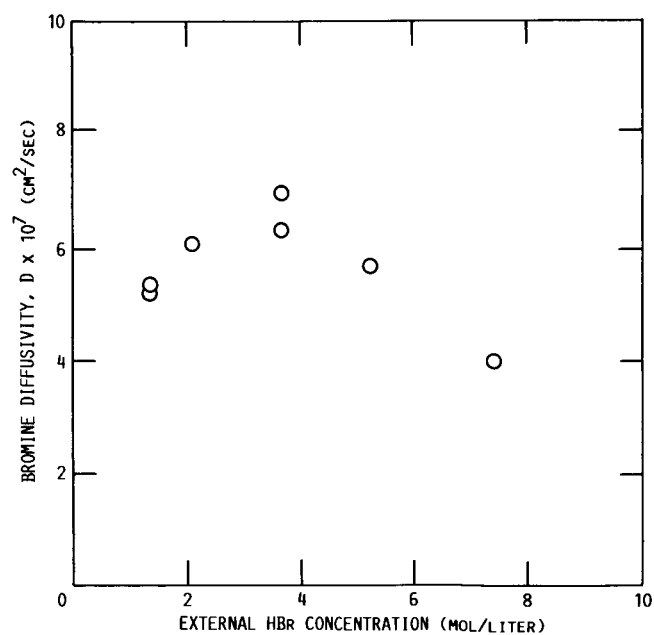

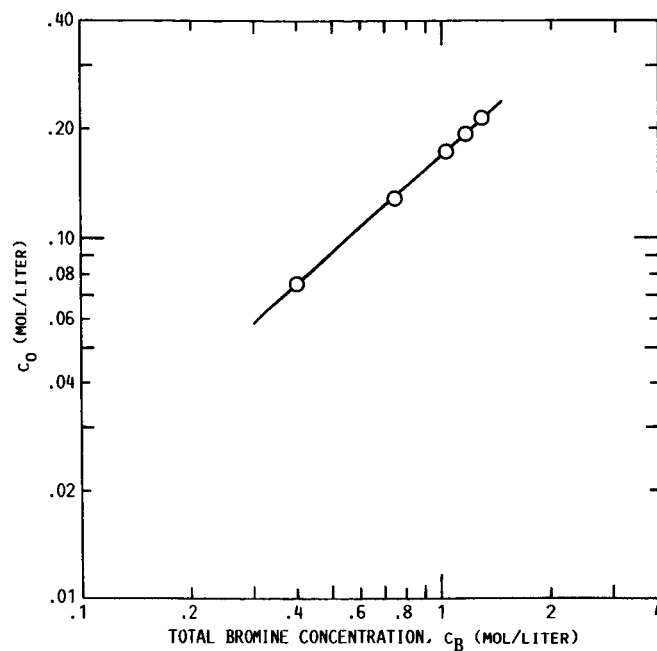FIGURE 10. - OBSERVED BROMINE DIFFUSIVITY IN NAFION-120 AT 25 ^{O}C AS A FUNCTION OF EXTERNAL HBr CONCENTRATION.

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FIGURE 11. - RELATIONSHIP OF c_0 TO c_B FOR BROMINE PERMEATION
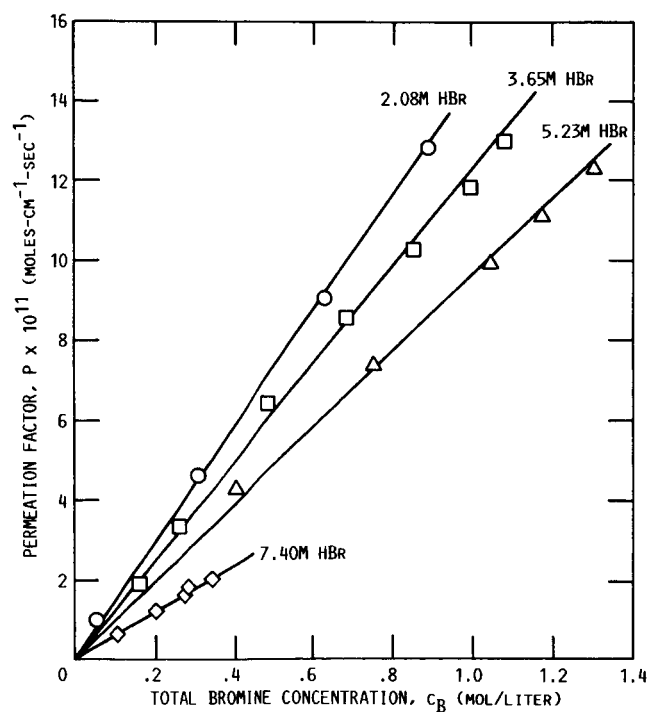THROUGH NAFION-120 IN 5.23M HBr AT 25 ^{0}C.

FIGURE 12. - PERMEATION FACTORS FOR OBSERVED BROMINE FLUXES
THROUGH NAFION-120 AT 25 ^{0}C AS A FUNCTION OF TOTAL
BROMINE CONCENTRATION AND EXTERNAL HBr CONCENTRATION.
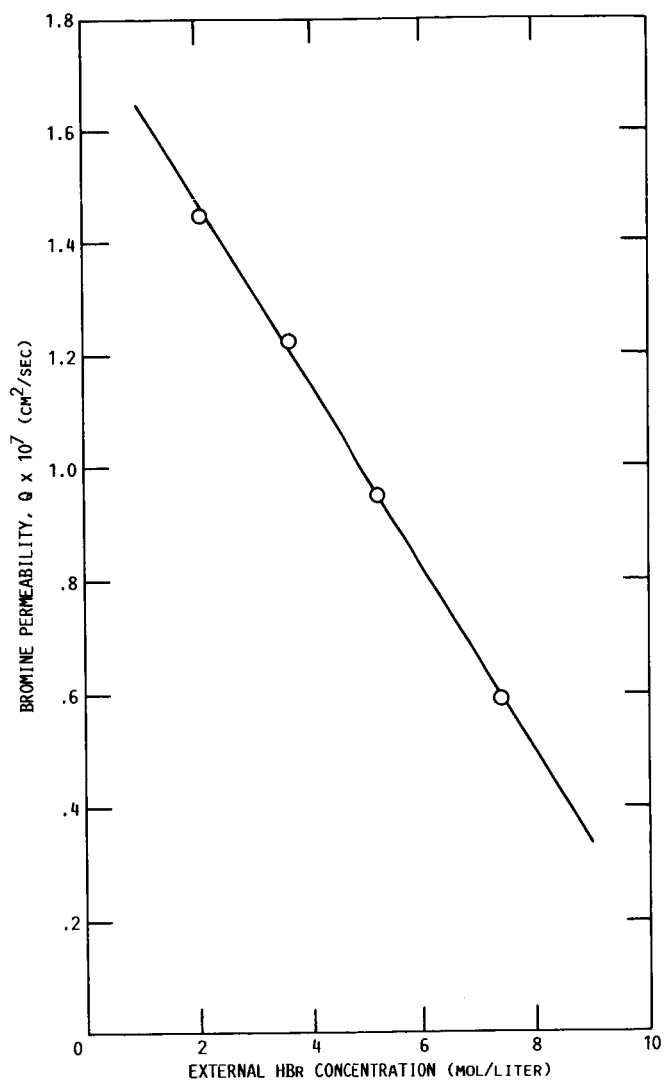
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FIGURE 13. - DEPENDENCE OF BROMINE PERMEABILITY UPON EXTERNAL
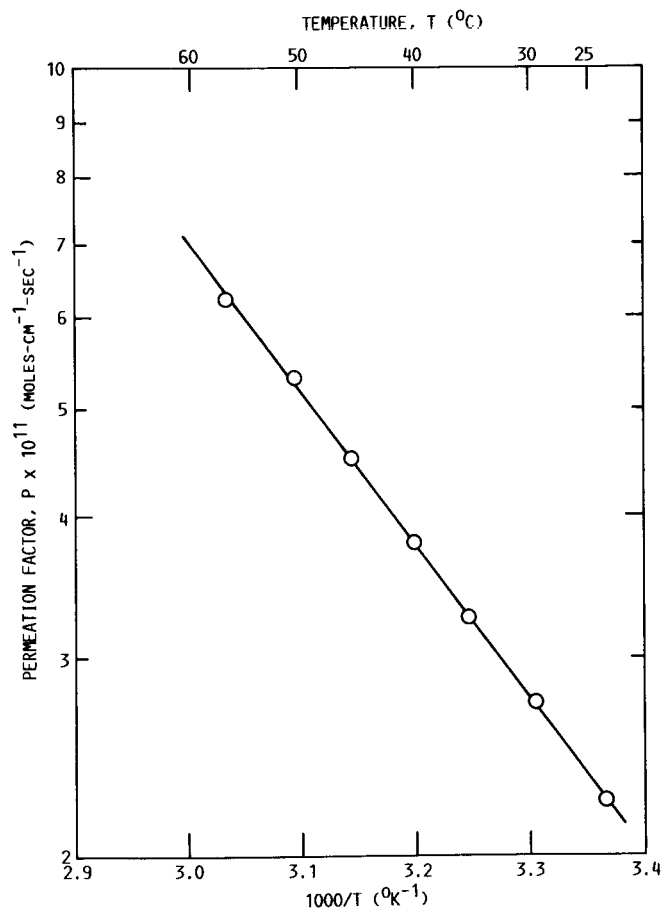HBr CONCENTRATION FOR PERMEATION THROUGH NAFION-120 AT
25 °C.

FIGURE 14. - TEMPERATURE DEPENDENCE OF BROMINE PERMEATION
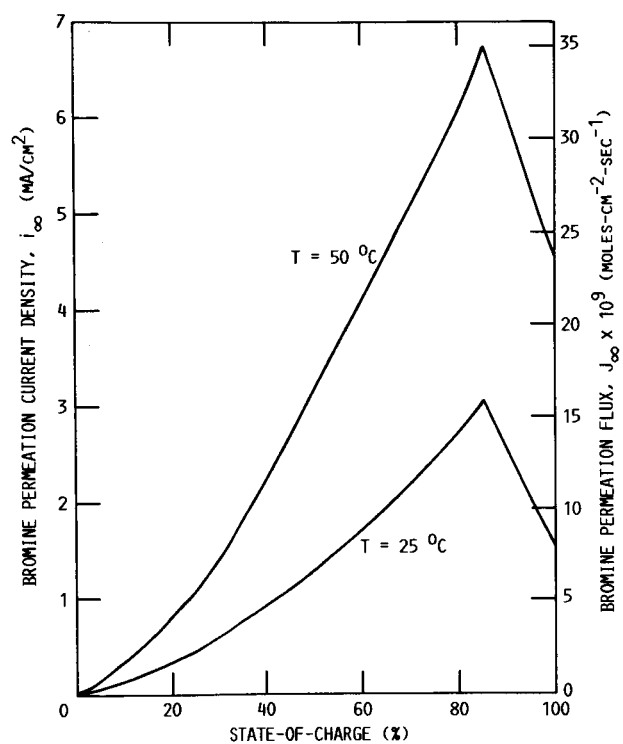FACTOR FOR NAFION-120 IN 5.22M HBr/0.23M Br$_2$.

FIGURE 15. - COMPUTED BROMINE PERMEATION CURRENTS THROUGH NAFION-120 AT 25 °C AND 50 °C AS A FUNCTION OF STATE-OF-CHARGE OF A H_2-Br_2 CELL BEING CHARGED FROM 45% HBr TO 5% HBr.

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15. Supplementary Notes

16. Abstract

The overall energy conversion efficiency of a hydrogen-bromine energy storage system is highly dependent upon the characteristics and performance of the ion-exchange membrane utilized as a half-cell separator. This study has investigated the electrochemical performance and transport properties of a duPont Nafion membrane in an aqueous $HBr-Br_2$ environment. Membrane conductivity data are presented as a function of HBr concentration and temperature for the determination of ohmic voltage losses across the membrane in an operational cell. Diffusion-controlled bromine permeation rates and permeabilities are presented as functions of solution composition and temperature. Relationships between the degree of membrane hydration and the membrane transport characteristics are discussed. The solution chemistry of an operational hydrogen-bromine cell undergoing charge from 45 percent HBr to 5 percent HBr is discussed, and, based upon the experimentally observed bromine permeation behavior, predicted cell coulombic losses due to bromine diffusion through the membrane are presented as a function of the cell state-of-charge.

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